09/526379

(11) (A) No. 1 125 229

(45) ISSUED 820608

(52) CLASS 204-91.34

(51) INT. CL. ^{3} C08J 3/28

(19) (CA) CANADIAN PATENT (12)

(54) IRRADIATED LAMINATE FILM HAVING HEAT SEALING CHARACTERISTICS

(72) Baird, William G., Jr.;
Engelmann, Alfred P.,
U.S.A.

(73) Granted to Grace (W. R.) & Co.
U.S.A.

(21) APPLICATION No. 337,225

(22) FILED 791009

(30) PRIORITY DATE U.S.A. (973,850) 781228

No. OF CLAIMS 14

DISTRIBUTED BY THE PATENT OFFICE, OTTAWA.
CCA-274 (3-80)

IRRADIATED LAMINATE FILM HAVING
HEAT SEALING CHARACTERISTICS

Abstract

A coextruded irradiated film has a crosslinked layer and a heat sealable layer. The crosslinked layer is crosslinked by irradiation at a dosage level sufficiently low that the heat sealing properties of the heat sealable layer are not adversely affected. The crosslinked layer is crosslinked to a desirable level due to the presence of irradiation crosslinking enhancers which are incorporated within the crosslinked layer so as to promote crosslinking at a low dosage level.

Background Of The Invention

The present invention relates generally to the art of crosslinked films and more particularly to the art of coextruded films having improved heat seal properties while simultaneously having the benefit of radiation induced crosslinking.

The use of heat shrinkable thermoplastic film in many packaging applications is well known. Usually a product is enclosed within a film, sealed and heated to shrink the film snugly about the product. One of the most useful and satisfactory thermoplastic materials for packaging film is polyethylene. In the prior art, there are a number of methods to convert polyethylene into suitable heat shrinkable packaging films. One such method is disclosed in U. S. Patent No. 2,855,517 to W. C. Ranier et al. Another method is disclosed in U. S. Patent No. 3,022,543 to W. G. Baird, Jr. et al. In the Baird, Jr. et al process, polyethylene is continuously extruded in the form of a tube, drawn, irradiated with electrons to crosslink the polyethylene molecules, heated and stretched again by applying internal pressure to the tubing. The resulting film from this proccess has highly desirable heat shrink properties.

It is generally known in the art that polymers and copolymers of olefins, particularly polyethylene, become thermosets if a sufficient radiation dosage is applied to the olefin object. For this reason it has been customary to form articles prior to an irradiation step in order to avoid the undesirable forming properties brought about by the transition from a thermoplastic to a thermosetting material. Also accompanying the transition from a thermoplastic to a thermosetting article is the progressively lessening ability of an olefin polymer article to heat seal to itself or to some other object as the radiation dosage is increased. For this reason it has generally been recognized in the film art that highly irradiated polyethylene films do not possess

the ability to form reliable high strength heat seals. The prior art has thus had to either rely upon a low radiation dosage in order to preserve heat sealing properties or to utilize a second layer or lamination which possesses desirable heat sealing properties and which is applied to the irradiated layer at some time after the process of irradiating.

Summary Of The Invention

It is thus an object of this invention to provide a novel film laminate which possesses the desirable characteristics associated with crosslinking brought about by irradiation while at the same time possessing heat sealing characteristics similar to those of non-irradiated articles.

The invention provides a process for producing a multi-layer irradiated structure having heat seal characteristics comprising the steps of:

providing a multi-layer structure having a crosslinkable layer including an irradiation enhancer and a heat sealable layer;

irradiating said multi-layer structure at a radiation dosage sufficient to crosslink said crosslinkable layer but insufficient to adversely affect the heat sealing characteristics of said heat sealable layer.

The invention also provides a coextruded multi-layer polymeric structure having a crosslinked layer including an irradiation crosslinking enhancer and a heat sealable layer.

Brief Description Of The Drawings

The single figure of drawing schematically illustrates a process for producing the coextruded laminate film of this invention.

Detailed Description

In accordance with this invention it has been found that it is possible to produce a coextruded laminate film structure which is crosslinked by irradiation while retaining the desirable heat sealing characteristics associated with non crosslinked structures within an outer layer of the laminate. This desirable combination of properties is brought about by incorporating into one of the layers of the laminate an irradiation crosslinking enhancer so as to greatly improve the crosslinking efficiency of the radiation utilized in the step of irradiating. The irradiation enhancer sufficiently lowers the necessary dosage level to a point at which the heat sealable layer is not adversely affected in its heat sealing characteristics by the incident radiation.

As used within this disclosure the term "polymer" is used with its normal meaning to include homopolymers, copolymers, terpolymers, etc. The term "crosslinking" is utilized to mean the union of polymer molecules by a mechanism involving primary chemical bonds to have the effect of binding a polymer into a single network so that functionally several molecules become bound together into a single molecule. As applied to polymers of mono-olefins particularly polymers and copolymers of ethylene, crosslinking is detectable by an increase in the remaining residue when the sample is contacted with toluene under reflux condition for about two days. This is generally referred to as the gel content. Thus, crosslinking is detected by an increase in the gel content of the crosslinked sample as compared to a non or lesser crosslinked sample.

As used within this disclosure, the term "irradiation crosslinking enhancer" is a chemical composition which when blended with a polymer in the melt form produces a material which crosslinks to a greater extent from a given radiation dosage than does the same polymer without the irradiation crosslinking enhancer additive. Thus an additive which when blended with a polymer to produce an irradiated crosslinked product having a higher gel content than the same polymer at the same radiation dosage level without the additive is an irradiation crosslinking enhancer.

In its broadest aspects the laminate of this invention comprises a core layer and a heat sealable layer which have both been through an irradiation step to crosslink the core layer to a high degree due to the presence therein of an irradiation crosslinking enhancer. The term "core" as used herein with reference to the core layer of the laminate of this invention is used to identify as an essential layer the layer which is crosslinkable, rather than to limit the core layer to a central or innermost layer. The laminate may comprise, however, additional layers such as additional heat sealing layers, or a layer to inhibit the passage of gaseous or liquid substances such as oxygen or moisture.

The core layer of the laminate of this invention is a polymer which is crosslinkable by irradiation and which may be enhanced in its crosslinking ability when blended with an irradiation crosslinking enhancer in accordance with this invention. Crosslinking using irradiation can be accomplished by various methods. Thus there can be used electrons, x-rays, and radiation of actinic origin such as ultraviolet light having a wave length above about 2,000 angstroms and below about 2,700 angstroms. Preferably, however, electrons of at least 10^5 electron volts energy are applied. The irradiation source can be a Van der Graaff type electron accelerator having an operational voltage of 2 megavolts at a power

output of about 5 to 10 kilowatts. Preferably, however, the source of electrons is an electron accelerator powered by an insulated core transformer having an accelerating voltage from about 300 to 3,000 kilovolts.

The absorbed radiation within the core layer is stated by the term "RAD". The RAD is defined as an energy dosage level of 100 ergs per gram imparted by the ionizing radiation to the irradiated material at the point of interest. The core material utilized in this invention, i.e., the polymer blended with the irradiation enhancer, is a material which will when blended with an enhancer undergo sufficient crosslinkage to increase the gel content thereof at a dosage level within the range of about 0.1 to about 5 megarads (MR).

The polymeric material with which is blended an irradiation enhancer to form the core layer of the laminate of this invention may be selected from a broad class of materials, i.e., those materials which crosslink when subjected to irradiation. While polymers of ethylene including copolymers thereof constitute the preferred material utilized within this invention, the invention may generally be carried out with polymers of other mono-olefins particularly the 1-alkenes and copolymers thereof. Particularly the invention may be carried out with polymers of propylene, butylene, pentene and hexene. The invention may additionally be carried out on vinyl chloride polymers and copolymers. The invention is particularly applicable to copolymers of ethylene and vinyl esters, e.g., vinyl acetate. The invention is applicable to any of the polymers of ethylene such as high and low density ethylene polymers produced by both high pressure and low pressure processes as well as mixtures and blends thereof.

Many irradiation crosslinking enhancers are known to the art. Any such enhancer may be utilized within the core layer of the laminate of this invention. While not meant to be limiting, the following is a

general listing of suitable classes of irradiation enhancers;

dialkyl maleates and fumarates in which the alkyl group contains 4 or more (usually 4 to 20) carbon atoms;

vinyl esters of fatty acids in which the fatty acid contains 3 or more (usually 3 to 20) carbon atoms;

vinyl alkyl ethers in which the alkyl group contains 18 or more (usually 18 to 30) carbon atoms;

alkyl acrylates in which the alkyl group contains 1 or more (usually from 1 to 20) carbon atoms; and

alkyl methacrylates in which the alkyl group contains 3 or more (usually from 3 to 20) carbon atoms.

Particularly preferred irradiation crosslinking enhancers for use with this invention are allyl methacrylate, allyl acrylate and diallyl maleate. The irradiation crosslinking enhancer can be incorporated into the core layer by several conventional techniques, e.g., mixing the materials from the powder form, blending the enhancer into the polymer in the molten state or by diffusing the irradiation crosslinking enhancer in the gaseous or liquid form into the solid polymer. It is preferred, however, to first mix the irradiation crosslinking enhancer in the powder form prior to melt blending the precursor of the core layer prior to melt extrusion. The irradiation enhancer in the solid polymer will not cause any crosslinking until the layer has been acted upon by a source of radiation as discussed above. The irradiation enhancer is normally employed in a small amount from about 0.05 to about 10 weight percent of the overall composition of the core layer, but in any event in an amount sufficient to increase the gel content of the core layer.

The heat sealable layer of the laminate film of this invention which is coextruded simultaneously with the extrusion of the core layer is of any material conventionally used for its heat sealing capability. Such materials generally heat seal to themselves at a temperature within the range of about 70 to about 150° C under a pressure from about 5

to about 50 lbs. per square inches (35 KPa to 350 KPa). Such materials then have a peel strength above 1 lb. per inch of width (17.9 kg/m) as measured by ASTM D-903. Such materials preferably have a peel strength above about 10 lbs. per inch of width (179 kg/m).

Materials which can be utilized for the heat sealable layer of the laminate of this invention include both high and low density polyethylene, polypropylene and other polymers of 1-mono-olefins. Particularly effective heat sealable substances include unsaturated ester polymers such as ethylene/unsaturated ester copolymers, e.g. ethylene/vinyl acetate, ethylene/vinyl propianate, ethylene/ethyl methacrylate, ethylene/ethyl methacrylate, ethylene/ethyl acrylate, ethylene/isobutyl acrylate, and the like; unsaturated carboxylic acid copolymers, e.g., ethylene/unsaturated carboxylic acid copolymers, e.g., ethylene/acrylic acid, ethylene/methacrylic acid, ethylene/maleic acid, ethylene/fumaric acid, ethylene/itaconic acid, and the like. The carboxylic acid groups of the acid copolymers may be either partly or wholly neutralized to form what is commonly referred to as an ionomer. Particularly preferred heat sealable materials are copolymers of ethylene and vinyl acetate containing from about 5 to about 40 weight percent of vinyl acetate. This listing, however, is not meant to be exhaustive but merely exemplary of the materials which might be utilized as a heat sealable layer within the laminate of this invention. These materials generally tend to diminish in their heat sealing ability upon exposure to irradiation sufficient to crosslink an otherwise non irradiation enhanced layer. By utilizing a core layer having an irradiation enhancer, however, the heat sealable layer is not exposed to sufficient radiation dosage to significantly deleteriously affect the heat sealing quality of the heat sealable layer.

The laminate film of this invention after being coextruded by conventional techniques is irradiated to a dosage level sufficient to enhance the mechanical and chemical properties of the core layer film without deleteriously affecting the heat seal qualities of the heat sealable layer. Preferably irradiation is carried out to a dosage level of about 0.1 to about 4 MR. This dosage level is sufficient to assure crosslinking within the core layer without adversely affecting the heat sealing characteristics of the heat sealable layer. One of the primary reasons for carrying out a crosslinking reaction is to enhance the ability of the core layer to undergo an orientation process so as to provide a heat shrinkable film. It is not necessary to the concept of this invention that an orientation process be carried out, however, since the irradiation crosslinking process enhances other desirable characteristics of the laminate film other than the ability to undergo orientation. It is preferred, however that the laminate film produced by this invention be oriented by conventional techniques so as to provide a film having heat shrink characteristics. It is especially preferred that such heat shrink characteristics exist at a temperature at or below the boiling point of water, i.e., 100°C. For purposes of this invention a laminate is biaxially oriented, if it exhibits a free shrinkage at 96°C of at least 10% in both the longitudinal and transverse directions.

The laminate of this invention is preferably produced by coextrusion of the materials in a tubular form as is generally described in U. S. Patent 3,874,967 to H. G. Schirmer commonly assigned herewith. The process of producing a laminate film of this invention is generally illustrated in the single figure of drawing. As is illustrated therein, two extruders, 2 and 3, are utilized for supplying coextrusion die 4 with various layers utilized for the laminate of this invention. Thus extruder 2 may be supplied with the core layer polymer including the irradiation enhancer and extruder 3 may be supplied with the heat

sealable layer of material. The extruders supply coextrusion die 4 so as to produce a tubular film 6. The die is positioned to extrude the tube downwardly into a cooling bath 8 of water or other inert liquid maintained at a temperature of between -18°C and +21°C. The cooled and flattened tubing of tape 16 is fed through feed rolls 18 into an irradiation vault 20 which houses and encloses a source of electrons 22. Following irradiation, the tape is fed by feed rolls 20 to a hot bath 30 in racking tank 46 which contains water or other liquid inert to the polymer layers. This liquid is maintained at a temperature sufficient to heat the tape to a desirable orientation temperature for the inner core layer. This temperature will vary somewhat depending upon the composition of the core layer. Orientation techniques are well known in the art, however, and a desirable orientation temperature is readily ascertainable for a particular polymer film material. For example, crosslinked low density polyethylene orients well at a temperature of about 88 to 102°C. The preferred temperature, however, is about 96°C. Air or other gasses are introduced into the heated tape to form a bubble 38 between the surface of the hot bath and the upper deflate rolls 34. The amount of inflation is preferably sufficient to provide a stretch of from about 3 to 1 to about 8 to 1 in each direction.

While the above description refers primarily to a coextruded laminate having only the two layers, it is readily apparent that other materials may be coextruded along with the two essential layers. The most readily extrudable layer would be an additional heat sealable layer identical in composition to the primary heat sealable layer in order to provide a three layer laminate which sandwiches the core layer. Other materials, however, such as layers to inhibit oxygen permeation, may be included along with the core and heat sealable layer or layers.

Having generally set forth the invention above, the following specific examples are given as a further exemplification of the laminate of this invention.

EXAMPLE I

Several samples were produced utilizing a core layer having incorporated therein an irradiation crosslinking enhancer in accordance with this invention. Structures comprising three concentric layers were coextruded from a 4 inch die utilizing an equal weight blend of high and low density polyethylenes within each layer. The central layer of the structures, however, contained a small percentage of diallyl maleate as an irradiation enhancer. All samples were oriented by the bubble technique at a temperature of approximately 250° F to provide a stretch of about 5 to 1 in both the machine and transverse directions. The samples were immediately chilled after orientation. Each of the samples had a thickness of about 1 mil (25 micrometers) after the orientation step. The properties of each sample as well as an identification of each sample is contained in the following table.

TABLE I

Sample No.	Layer Ratio	Irradiation Level MR	Wt. % Diallyl Malleate	Shrink Tension (psi) Transverse		Shrink Tension (psi) Longitudinal		Free Shrink % (Longitudinal)		Free Shrink % (Transverse)	
				200°F	300°F	200°F	300°F	200°F	300°F	200°F	300°F
1	1/2/1	2	0.3	439	300	189	249	6	83	12	78
2	1/1/1	3	0.2	377	388	242	326	8	82	12	79
3	1/1/1	3.5	0.3	481	357	173	274	6	82	12	80
4	1/1/1	4	0.3	332	415	324	341	8	81	10	78

EXAMPLE II

Two samples were produced utilizing a core layer having incorporated therein an irradiation crosslinking enhancer in accordance with this invention. The two structures were produced of the same material in substantially the same way as the samples in Example I. Samples 3 and 4 were produced of polyethylene blends similar to the blends utilized in samples 1 and 2 but did not contain an irradiation crosslinking enhancer and were produced as a single layer having a thickness comparable to that of samples 1 and 2. All samples had a total thickness of about 0.75 mils (about 19 micrometers). The coextruded structures had layers of equal thickness.

The gel content of each sample was determined by refluxing samples in toluene for 21 hours in order to insure complete solution of all soluble portions. This data is tabulated in Table II along with an identification of the samples, the dosage and an indication as to whether the gel content was determined from the outer heat sealable layer or core layer. It should be noted that the outer layers of the samples having no irradiation crosslinking enhancer had no gel while the core layer which contained the enhancer had gel percentages higher than sample no. 3 which contained no irradiation crosslinking enhancer. Samples 1 through 4 were tested for seal strengths utilizing ASTM standard F88-68 for both lap seals and trim seals at various electric current levels within the heating element. The lap seals were formed using a nickel-chromium heating ribbon covered with a sheet of polytetrafluoroethylene. The heating ribbon was operated in impulse fashion using a 2 second heating and 2 second cooling cycle. The trim seals were formed using a heating wire of the same alloy heated continuously with a six second interval between trim seals. The data are tabulated in Tables 3 and 4 along with some retabulation of identifying data from Table 2. It is seen that the seal strength of the highly irradiated samples 3 and 4 is significantly less at comparable amperage than the lesser irradiated samples containing a core layer with an irradiation crosslinking enhancer.

TABLE II

Sample No.	Structure	Dosage MR	% Diallyl Malleate	% Gel Total Structure	% Gel Skin	% Gel Core
1	1/1/1	2	0.2	3.8	0	12
2	1/1/1	3	0.3	5.4	0	16
3	single layer 0.75 mil	5	0	5.4	-	5.4
4	single layer 0.75 mil	10	0	42.6	-	42.6

TABLE III

Sample	Structure	Dosage MR	% DAM	Seal Strength (Lap Seals)							
1	1/1/1	2	0.2	Amperage	22	24.2			26.3		28.7
				Strength (lb)	0.42	0.87			3.01		3.22
2	1/1/1	3	0.3	Amperage	21.9	24.4			26.5		
				Strength (lb)	0.35	1.14			3.25		
3	1	5	0	Amperage	22.5	23.5	25.3	25.7		27.8	28
				Strength (lb)	0.72	0.58	1.11	2.13		2.41	3.22
4	1	10	0	Amperage	23		25.2	-		27.5	-
				Strength (lb)	0.74		1.66	-		1.99	-

TABLE IV

Sample No.	Dosage (MR)	Trim Seal Strength (lb)				
1	2	Amperage	-	7.3	8.0	8.8
		Strength	-	5.66	5.14	2.93
2	3	Amperage	6.9	7.6	8.3	-
		Strength	5.76	5.48	4.30	-
3	5	Amperage	6.7	7.4	8.1	-
		Strength	5.58	4.80	3.47	-
4	10	Amperage	-	-	8.3	9.1
		Strength	-	-	1.73	1.65

1125229

It is thus seen that the laminate of this invention and the process by which it is produced provides a multi-layer structure which has all of the desirable attributes of a crosslinked structure without the corresponding deleterious effect on heat sealing characteristics.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A coextruded multi-layer polymeric structure having a crosslinked layer including an irradiation crosslinking enhancer and a heat sealable layer.

2. The multi-layer structure according to claim 1 wherein said heat sealable layer has heat sealing characteristics substantially similar to a non-irradiated layer of the same material.

3. The multi-layer structure of claim 1 wherein said crosslinked layer is a polymer of a 1-mono-olefin.

4. A multi-layer structure according to claim 3 wherein the irradiation enhancer is a material selected from the group consisting of dialkyl maleates, dialkyl fumarates, vinyl esters of fatty acids, vinyl alkyl ethers, alkyl acrylates, and alkyl methacrylates.

5. A multi-layer structure according to claim 4 wherein said irradiation enhancer is selected from the group consisting of allyl methacrylate, allyl acrylate and diallyl maleate.

6. The multi-layer structure according to claim 1, 2 or 3 wherein the heat sealable layer is sealable at a temperature in the range of 70 to 150°C at a pressure of about 5 to about 50 psi to produce a seal having a peel strength of greater than about 1 lb. per inch of width.

7. The multi-layer structure of claim 1 in the biaxially oriented state.

8. The multi-layer structure of claim 7 with a free shrinkage of at least 10% in both axial and transverse directions at 96°C.

9. A process for producing a multi-layer irradiated structure having heat seal characteristics comprising the steps of:

providing a multi-layer structure having a crosslinkable layer including an irradiation enhancer and a heat sealable layer;

irradiating said multi-layer structure at a radiation dosage sufficient to crosslink said crosslinkable layer but insufficient to adversely affect the heat sealing characteristics of said heat sealable layer.

10. The process according to claim 9 wherein said step of irradiating is carried out so as to provide a dosage level within the range of 0.1 to about 4 MR.

11. The process according to claim 9 wherein said crosslinkable layer is a polymer of a 1-mono-olefin.

12. The process according to claim 9 wherein the irradiation enhancer is selected from the group consisting of dialkyl maleate, dialkyl fumarates, vinyl esters of fatty acids, vinyl alkyl ethers, alkyl acrylates and alkyl methacrylates.

13. The process according to claim 12 wherein said irradiation enhancer is selected from the group consisting of allyl methacrylate, allyl acrylate and diallyl maleate.

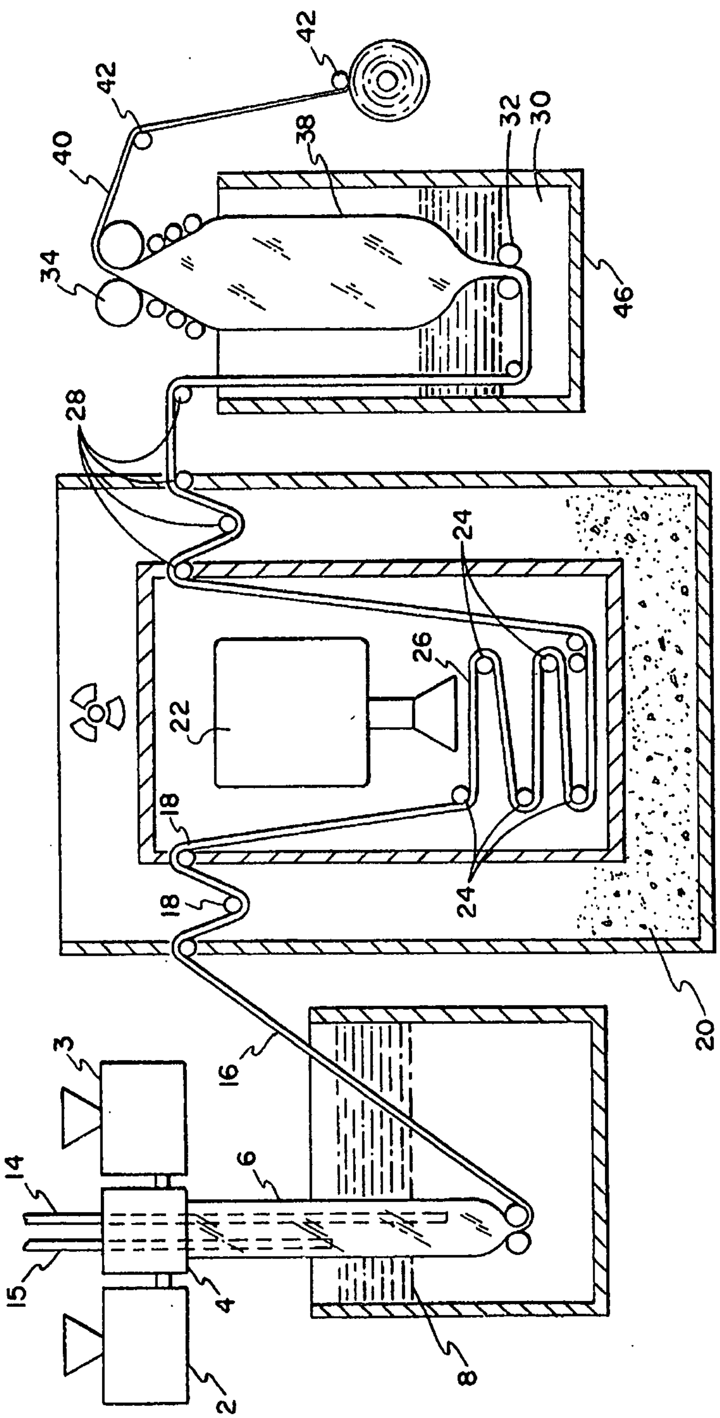
14. The process of claim 9, 10 or 11 including the further step of orienting said multi-layer structure.

SMART & BIGGAR
OTTAWA, CANADA

PATENT AGENTS

B

1125229



Patent Agents